Temperature, absorption and excitation study of the $A_{1-x}B_xC$ crystals by Raman scattering method

M. Kozielski, M. Szybowicz

Faculty of Technical Physics, Poznan University of Technology,
Piotrowo 3, 60-965 Poznań, Poland

ABSTRACT

Recently, wide gap II-VI mixed crystals are studied for their application in technology of blue-green laser diodes. The mixed crystals were growth using the modified pressure Bridgman method.

The temperature, absorption and excitation study of $Zn_{1-x}A_xSe$ mixed crystals using Raman scattering method is reported. Measurements have been performed for crystals with $x = 0.07$ for A = Mg content and $x = 0.09$ for A = Be content. The Raman scattering spectra were obtained for different temperatures and different excitation wavelengths.

From the Raman spectra the longitudinal optical (LO) and transverse optical (TO) modes which correspond to ZnSe-, MgSe- and BeSe-like single crystals were distinguished. For all used excitation wavelengths and different temperatures the integrated intensities of LO and TO modes using a curve-fitting method have been calculated.

Keywords: Raman scattering, mixed crystals, optical phonons.

1. INTRODUCTION

Recently, the physical properties of wide-gap II-VI mixed crystals have been extensively studied using different experimental techniques.[1,2] These crystals are of significant interest for their potential applications in technology of blue semiconductor lasers. In order to construct such a devices, the proper band structure modulation has to be obtained. This may be achieved with the use of ternary alloys. The mixed crystals based on II-VI compounds offer direct band gap through the entire visible spectral range up to the ultraviolet.

In this paper the study of the vibrational modes in $Zn_{1-x}Mg_xSe$ and $Zn_{1-x}Be_xSe$ mixed crystals using Raman scattering method are reported. Semiconductor crystals were measured at room temperature (RT) and liquid nitrogen temperature (LNT), for various excitation wavelengths. We have also estimated the temperature dependence of the integrated intensity ratio $I_{LO}^{ZnSe} / I_{TO}^{ZnSe}$ for both crystals and for different excitation lines. Some results concerning Raman investigations performed at RT and LNT for $Zn_{1-x}Mg_xSe$ and $Zn_{1-x}Be_xSe$ have been recently published.[3,4,5]

2. EXPERIMENT

The $Zn_{1-x}Mg_xSe$ and $Zn_{1-x}Be_xSe$ crystals were grown by the modified Bridgman method described in details elsewhere.[6] The mixed crystals composition was determined by electron microprobe ($Zn_{1-x}Mg_xSe$) and chemical wet ($Zn_{1-x}Be_xSe$) analysis. The measurements were performed for mixed crystals in the composition $x = 0.07$ for $Zn_{1-x}Mg_xSe$ and $x = 0.09$ for $Zn_{1-x}Be_xSe$. The samples used in Raman scattering experiment were ground and polished to the optical quality. The Raman measurements were performed with the use of the helium cryostat (Optistat^{CF} static continuous flow cryostat). The Raman spectra were measured for various excitations wavelength (458 nm, 477 nm, 488 nm, 497 nm and 515 nm). The scattered radiation was analysed with a double-grating monochromator and detected by a cooled EMI photomultiplier, followed by a photon counting system. The experimental setup permitted the band positions of Raman spectra to be estimated with an accuracy of ± 2 cm^{-1}.

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3. RESULTS AND DISCUSSION

Vibrational Raman spectra of $Zn_{1-x}Mg_xSe$ and $Zn_{1-x}Be_xSe$ for various excitation wavelengths obtained at room temperature are presented in Fig. 1. The typical spectrum consists of ZnSe-like and MgSe-like modes for $Zn_{1-x}Mg_xSe$ crystals, and ZnSe-like and BeSe-like modes for $Zn_{1-x}Be_xSe$ crystals. Both crystals being under study show a typical two-mod behaviour. This problem was described in details in our previous works.[7,8]

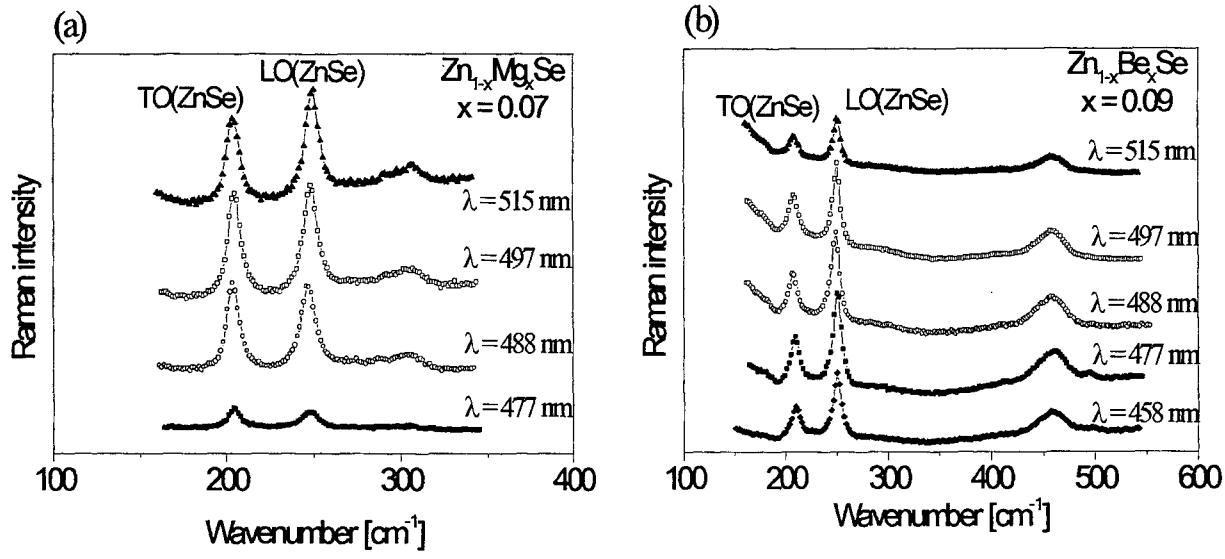

Fig. 1. The Raman spectra of $Zn_{1-x}Mg_xSe$ and $Zn_{1-x}Be_xSe$ crystals obtained for different excitation lines at room temperature.

As it can be seen from Fig. 1a for $Zn_{1-x}Mg_xSe$ crystals the increase of excitation wavelength induces increasing of $LO_{ZnSe\text{-}like}$ and $TO_{ZnSe\text{-}like}$ Raman integrated intensities. For excitation wavelength λ_{exc} = 515 nm the integrated intensity of LO mode is larger than TO mode. For λ_{exc} = 477 nm the integrated intensity of $LO_{ZnSe\text{-}like}$ mode is smaller than $TO_{ZnSe\text{-}like}$ mode. In the case of $Zn_{1-x}Mg_xSe$ crystal integrated intensities of LO and TO modes corresponding to ZnSe-like mode increase with increasing of the excitation wavelength. There is no Raman spectra observed at room temperature for excitation wavelength λ_{exc} = 458 nm.

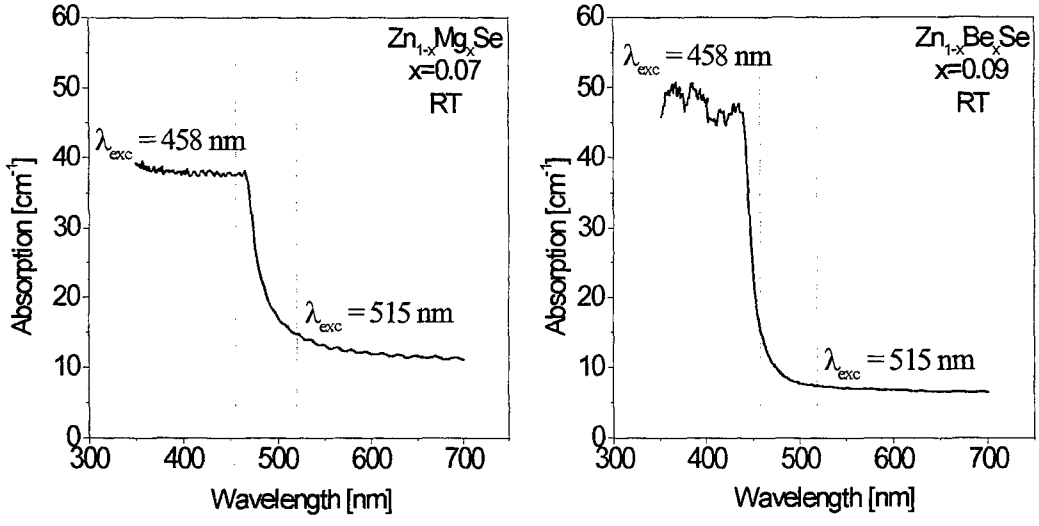

Fig. 2. The absorption of $Zn_{1-x}Mg_xSe$ and $Zn_{1-x}Be_xSe$ crystals as a function of excitation wavelength at room temperature.

The increase of the intensity of Raman bands versus excitation wavelength can be reasoned by considering the dependence of the light absorption in the crystals (see Fig. 2a). As it can be seen from Fig. 2a there is no possibility to observe the Raman spectrum for excitation line 458 nm due to great absorption in the crystal for this wavelength. With the increase of the excitation wavelength the absorption in the crystal decreases and in consequence the integrated intensity of Raman bands increases.

There is different behaviour of the intensity of the LO and TO modes for $Zn_{1-x}Be_xSe$ and $Zn_{1-x}Mg_xSe$ crystals. The Fig. 2b shows that at room temperature the intensity of the $LO_{ZnSe\text{-}like}$ and $TO_{ZnSe\text{-}like}$ modes for $Zn_{1-x}Be_xSe$ crystals have almost the same value for various excitation lines. The biggest intensity is observed for excitation wavelength λ_{exc} = 477 nm and the lowest intensity for line λ_{exc} = 515 nm. For $Zn_{1-x}Be_xSe$ crystals the excitation line λ_{exc} = 477 nm is not situated on absorption edge (see Fig. 2b). At it can be seen from Fig. 2b the excitation line λ_{exc} = 515 nm is located at small absorption range, causing the lower intensity the LO and TO modes in the Raman spectrum.

We have also analysed the behaviour of integrated intensities of the $LO_{ZnSe\text{-}like}$ and $TO_{ZnSe\text{-}like}$ modes as a function of temperature and excitation wavelength. The estimated temperature dependence of the integral intensity ratio $I_{LO}^{ZnSe} / I_{TO}^{ZnSe}$ as a function of excitation wavelength is presented in Fig. 3.

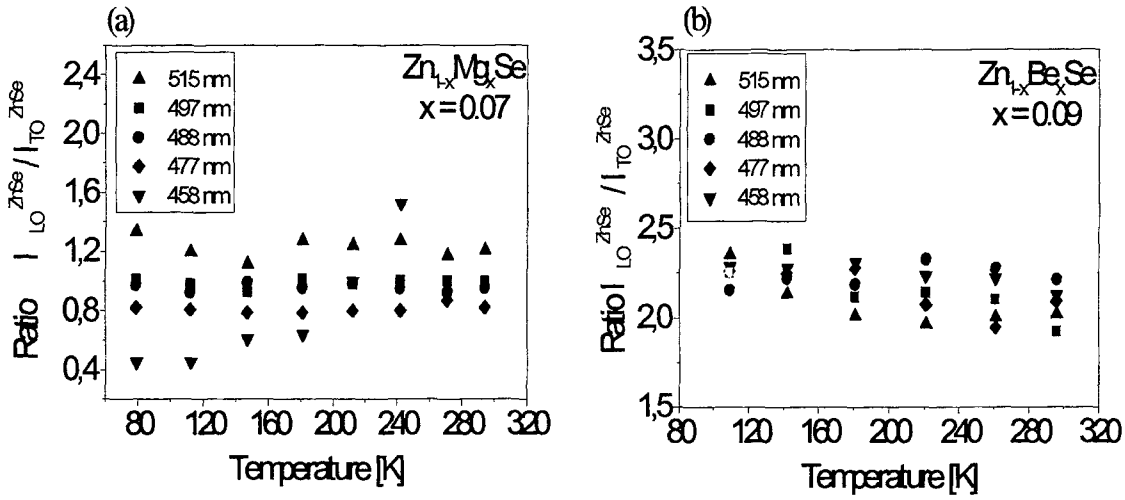

Fig. 3. The temperature dependence of the integral intensity ratio $I_{LO}^{ZnSe} / I_{TO}^{ZnSe}$ for $Zn_{1-x}Mg_xSe$ and $Zn_{1-x}Be_xSe$ crystals obtained for different excitation wavelength.

As it can be seen from Fig. 3a for $Zn_{1-x}Mg_xSe$ crystals the Raman spectra for excitation line λ_{exc} = 458 nm appears at 241 K. For these crystals the integrated intensity ratio $I_{LO}^{ZnSe} / I_{TO}^{ZnSe}$ for excitation lines: 477 nm, 488 nm, 497 nm and 515 nm through the temperature range is constant. Figure 3a also shows that with the increase of excitation wavelength the integrated intensity ratio $I_{LO}^{ZnSe} / I_{TO}^{ZnSe}$ increases. However, for λ_{exc} = 458 nm we observe an increase of the integrated intensity ratio $I_{LO}^{ZnSe} / I_{TO}^{ZnSe}$ while the temperature is increasing. For $Zn_{1-x}Be_xSe$ crystals the temperature dependence of the integrated intensity ratio $I_{LO}^{ZnSe} / I_{TO}^{ZnSe}$ for all excitation lines is constant (see Fig. 3b).

3. CONCLUSIONS

The Raman study of $Zn_{1-x}Mg_xSe$ and $Zn_{1-x}Be_xSe$ mixed crystals has been performed for various temperatures and different excitation wavelengths. The temperature dependence of the integrated intensity ratio $I_{LO}^{ZnSe} / I_{TO}^{ZnSe}$ for ZnSe-like modes should be considered in terms of the absorption for these crystals. The increase in the value of $I_{LO}^{ZnSe} / I_{TO}^{ZnSe}$ with increasing of the excitation wavelength can be attributed to the different penetration depth in the crystal. Interaction of the LO phonon field with the surface electric field causes the increase of the intensity ratio $I_{LO}^{ZnSe} / I_{TO}^{ZnSe}$.

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